## Catalysis Phenomena and Intermediates in the Reaction of Phosphorus Trichloride with Aldehydes

Mukattis B. Gazizov,<sup>a</sup> Rafail A. Khairullin,<sup>a</sup> Roza F. Kadirova,<sup>a</sup> Edward S. Lewis,<sup>b</sup> and Alan M. Kook<sup>b</sup>

<sup>a</sup> The Kirov Institute of Chemical Technology, 420015 Kazan, K. Marx st., 68, USSR <sup>b</sup> Rice University, Houston, Texas 77251, USA

Both hydrogen chloride and tertiary amines have been found to catalyse the reaction of  $PCl_3$  with aldehydes; two types of intermediate not previously observed have been synthesized.

The phosphite structures (4) have been postulated as intermediates in the reaction of phosphorus trichloride (1) with aldehydes (2).<sup>1</sup> Miller *et al.* proposed that (4a) should react rapidly with a second aldehyde molecule to give 1-chloro-1chloroalkoxyalkanes (6).<sup>2</sup> The phosphite structure (5) was expected to be the precursor of (6).

Commercial phosphorus trichloride (1) was found to be

contaminated with HCl, even after multiple distillation. The HCl can be removed from commercial (1) and other P<sup>III</sup> chlorides by treatment with N, N-diethylaniline.<sup>†</sup> Refined (1)

<sup> $\dagger$ </sup> Compound (1) and tertiary amine (3) were mixed in a 1:0.15 ratio and PCl<sub>3</sub> was distilled directly into the reaction flask.

does not react with aldehydes (2) except for a slow aldehyde trimerisation, whereas under the same conditions commercial (1) reacts exothermically with (2), owing to catalysis by HCl. In turn a small amount of a tertiary amine (triethylamine, N,N-dimethyl- or diethyl-anilines, pyridine, or 2,6dimethylpyridine) (3) gives rise to a violent reaction of (2) with purified (1) showing base catalysis. We have found that the addition of one or two molecules of (2) to one P-Cl bond depends on the concentration of amine (3). When 1-5% of (3) is used, the adduct (4a) derived from the addition of one molecule of (2) is formed (Scheme 1). We suppose that (3) not only makes the carbonyl oxygen more reactive but also protects its electrophilic centre from the addition of a second aldehyde molecule. For the synthesis of (4a) the best ratio of the starting materials (1), (2), and (3) is 1:1:0.02-0.05. Aldehyde (2) was added dropwise to the mixture of purified (1) and amine (3) at -5 °C. Compounds (4a; R = Pr<sup>n</sup>, Pr<sup>i</sup>) were separated by vacuum distillation (56.6, 53.3%, respectively) and the structure of (4a; R = Me), which could not be readily isolated by distillation, was confirmed by its NMR spectra‡ and by transformation into stable (7),‡ (8a), and (9a) by treatment with trimethyl orthoformate, dimethyl sulphoxide, and 1,1-dimethoxyethane, respectively.

When the amount of (2) is increased the substitution of chlorine atoms turns out to be nonselective. Thus when the ratio of (1):(2):(3) is 1:2:0.01 the composition of the reaction mixture (ascertained by <sup>31</sup>P NMR spectroscopy) is 5.4% (1), 39.9% (4a), and 55.3% (4b), and when the ratio is 1:4:0.05 then the mixture contains 3.1% (4a), 24.8% (4b),

Selected data for (**4a**; R = Me): <sup>1</sup>H NMR  $\delta$  1.81 (d, J 5.6 Hz, Me), 6.38 (dq, J 5.6, 13.9 Hz, CH); <sup>13</sup>C NMR  $\delta$  27.88 (s, Me), 86.06 (d, J 10.6 Hz, CH); <sup>31</sup>P NMR  $\delta$  178.1, 177.7 ppm. (**4a**; R = Pr<sup>i</sup>): b.p. 30 °C (0.01 mmHg),  $d_4^{20}$  1.3029; <sup>1</sup>H NMR  $\delta$  1.08, 1.06 (d, J 6.7 Hz, 2Me), 2.20 (d. hept, J 6.7, 3.8 Hz, CH), 6.13 (dd, J 3.8, 14.4 Hz, CH); <sup>13</sup>C NMR  $\delta$  17.27, 16.43 (s, Me), 36.87 (s, CH), 94.4 (d, J 10.04 Hz, CH); <sup>31</sup>P NMR  $\delta$  179.61 and 179.24 (3:1).

(7; R = Me): b.p. 91 °C (0.01 mmHg),  $d_4^{20}$  1.2444; <sup>1</sup>H NMR  $\delta$  1.56, 1.54 (d, J 5.1, 5.6 Hz, Me), 3.23 (m, 2MeO), 3.56, 3.57 (d, J 10.7, 10.5 Hz, POMe), 4.42, 4.40, 4.35, 4.37 (d, J 7.3, 7.4, 6.6, 6.6 Hz, CHO<sub>2</sub>), 6.05 (m, CHCl); <sup>13</sup>C NMR  $\delta$  26.92, 27.24 (d, J 7.10, 5.99 Hz, Me), 56.31, 56.16, 55.73, 55.68 [d, J 11.7, 11.2, 11.50, 11.50 Hz, C(OMe)<sub>2</sub>], 52.92, 52.88 (d, J 6.7, 6.7 Hz, POMe), 84.74, 84.41 (d, J 6.5, 8.0 Hz, CHCl), 100.69, 99.90 (d, J 206.9, 211.4 Hz, CHO<sub>2</sub>); <sup>31</sup>P NMR  $\delta$  14.73, 14.42 ppm.

(9a;  $\hat{\mathbf{R}} = \text{Me}$ ): b.p. 51—52 °C (0.04 mmHg),  $d_4^{20}$  1.1940; <sup>1</sup>H NMR  $\delta$  1.25 (dd, J 18.0, 7.0 Hz, PCHMe), 1.75 (d, J 5.6 Hz, MeCHCl), 3.35 (s, OMe), 3.75 (d, J 12.0 Hz, POMe), 6.11 (m, CHCl); <sup>31</sup>P NMR  $\delta$  25.0 ppm.

(9b; R = Pr<sup>n</sup>): b.p. 80—82 °C (0.03 mmHg),  $d_4^{20}$  1.1439; <sup>1</sup>H NMR  $\delta$  0.83 (t, J 6.3 Hz, MeCH<sub>2</sub>), 1.22—1.42 (m, MeCH and MeCH<sub>2</sub>), 1.92 (m, CH<sub>2</sub>CH), 3.37 (s, OMe), 3.70, 3.65 (d, J 10.0 Hz, POMe), 6.11 (m, CH); <sup>13</sup>C NMR  $\delta$  11.2 (s, MeCH<sub>2</sub>), 12.7, 13.1 (s, MeCH<sub>2</sub>), 40.6 (s, CH<sub>2</sub>CH), 50.8 (d, J 8.0 Hz, CHOMe), 56.9 (d, J 8.0 Hz, POMe), 71.7, 72.0, 72.3 (d, J 168, 162, 166 Hz, CHOMe), 86.7, 87.1 (d, J 10.0 Hz, CHCl); <sup>31</sup>P NMR  $\delta$  25.0 ppm.

(8b; R = Me): b.p.  $62^{\circ}$ °C (0.01 mmHg),  $d_4^{20}$  1.4031; <sup>1</sup>H NMR  $\delta$  1.79 (m, Me), 6.28 (m, CH); <sup>13</sup>C NMR  $\delta$  86.32, 86.23 (d, J 9.7, 8.7 Hz, CH), 27.02, 26.98 (d, J 9.8, 9.8 Hz, Me); <sup>31</sup>P NMR  $\delta$  2.42, 1.20, and 0.72 ppm (1.0:0.5:0.5).

Satisfactory elemental analysis were obtained for all compounds characterised.



$$Cl_2POCH(R)OCH(R)Cl \xrightarrow{Cl_2} POCl_3 + RCH(Cl)OCH(Cl)R$$
(5)
(6)

Scheme 1

MeCH(Cl)O(MeO)P(O)CH(OMe)<sub>2</sub>  
(7)  
[MeCH(Cl)O]<sub>n</sub>P(O)Cl<sub>3-n</sub>  
(8) 
$$\mathbf{a}$$
;  $n = 1$   
 $\mathbf{b}$ ;  $n = 2$ 

RCH(Cl)O(MeO)P(O)CH(OMe)Me(9) a; R = Me
b; R =  $Pr^n$ 

and 72.1% (4c). Both (4b) and (4c) revert to (1) and (2) on heating, thus the reactions are reversible. The structures of (4b; R = Me) and (4c; R = Me) were confirmed by their NMR spectra§ and their transformation into stable (8b)‡ with dimethyl sulphoxide or phosphorus pentachloride.

We suspected that there might be a minimum concentration of (3) at which its ability to protect the electrophilic centre of the carbonyl group would be weakened, although it would still function as a catalyst. Indeed, when the ratio (1):(2):(3) is 1:1 (or 2):0.0075-0.008 then the second type of intermediate (5; R = Me) is formed, as shown by NMR spectroscopy.¶ <sup>31</sup>P NMR data shows that its content in the reaction mixture is 22%, or 47% when a twofold excess of (2) is used. Intermediate (5) is stable at -20 to -30 °C but, at temperatures higher than -10 °C, it easily decomposes into 1-chloro-1-chloroethoxyethane (6), prepared previously by Miller *et al.*<sup>2</sup> The intermediates (5; R = Pr<sup>n</sup> and Pr<sup>i</sup>) react with chlorine to produce (6) and POCl<sub>3</sub>.

Received, 14th February 1990; Com. 0/00684J

## References

- 1 H. J. Page, J. Chem. Soc., 1912, **101**, 423; M. I. Kabachnik, Russ. Chem. Rev., 1947, **16**, 402; F. R. Atherton, V. M. Clark, and A. R. Todd, Recl. Trav. Chim. Pays-Bas, 1950, **69**, 295.
- 2 J. A. Miller and M. J. Nunn, J. Chem. Soc., Perkin Trans. 1, 1976, 535; Tetrahedron Lett., 1972, 3953.

¶ <sup>1</sup>H *NMR* data for (5; R = Me):  $\delta$  1.56 (d, J 5.15 Hz, Me), 5.92 (dq, J 5.15, J<sub>PH</sub> 12.47 Hz, CH), 1.73 (d, J 5.50 Hz, Me), 5.75 (q, J 5.50 Hz, CH); <sup>13</sup>C NMR  $\delta$  22.68 (s), 98.64, 98.47 (d, J 4.36 Hz, MeCHO<sub>2</sub>), 25.90 (s), 88.67, 88.60 [s, MeCH(Cl)O]; <sup>31</sup>P NMR  $\delta$  169.62, 169.31 ppm.

 $<sup>^{\</sup>ddagger}$  <sup>1</sup>H (300 MHz), <sup>13</sup>C (75.5 MHz), and <sup>31</sup>P (121.5 MHz) NMR spectra were recorded on a 7.0 T IBM/ Bruker AF 300 NMR spectrometer in CDCl<sub>3</sub> (G = 10<sup>-4</sup> T) using Me<sub>4</sub>Si as internal and 85% H<sub>3</sub>PO<sub>4</sub> as external standard.

<sup>§ &</sup>lt;sup>1</sup>H *NMR* data for (**4b**):  $\delta$  1.83 (d, *J* 6.4 Hz, Me), 6.14 (m, CH); (**4c**):  $\delta$  1.81 (d, *J* 5.6 Hz, Me), 6.14 (m, CH); <sup>13</sup>C NMR for (**4b**):  $\delta$  27.66, 27.51 (s, Me), 84.66, 84.56 (d, *J* 8.2, 5.3 Hz, CH); (**4c**):  $\delta$  27.56—27.77 (m, Me), 84.11—84.52 (m, CH); <sup>31</sup>P NMR for (**4b**)  $\delta$  163.32, 162.97, 162.43 ppm; (**4c**):  $\delta$  145.87, 138.32 ppm.